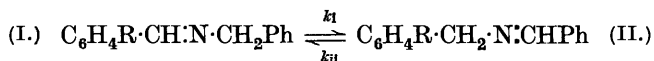**88.** *Symmetrical Triad Prototropic Systems. Part VIII. The Analogy between Symmetrical Triad Systems and Aromatic Side-chain Reactivity, and the Effect of* m-*Substitution on Mobility and Equilibrium in the* αγ-*Diphenylmethyleneazomethine System.*

By Charles William Shoppee.

In Part VII (J., 1931, 1225) attention was directed to the analogy existing between facilitation by nuclear substituents of (*a*) aromatic side-chain reactivity requiring electron recession ("type B" of Ingold and Rothstein; J., 1928, 1217) and (*b*) mobility in simple triad prototropic systems activated by aromatic residues. An examination was made of the influence of a series of *p*-substituents (R = Me, Cl, Br, I, OMe, NMe$_2$, $\overset{\oplus}{N}$Me$_3$) on mobility and equilibrium in the αγ-diphenylmethyleneazomethine system (I $\rightleftharpoons$ II) and the results were correlated with the influence of the same *p*-substituents on side-chain reactivity of type B.

The influence of a parallel series of *m*-substituents (R = Me, Cl, Br, I, OMe, NMe$_2$, $\overset{\oplus}{N}$Me$_3$, $\overset{\oplus}{N}\!\!<^{O\ominus}_{O}$) on mobility and equilibrium in the system (I $\rightleftharpoons$ II) is now recorded, and compared with the influence of the same *m*-substituents on side-chain reactivity of type B.

$$\text{(I.)} \quad C_6H_4R\cdot CH:N\cdot CH_2Ph \underset{k_{ii}}{\overset{k_i}{\rightleftharpoons}} C_6H_4R\cdot CH_2\cdot N:CHPh \quad \text{(II.)}$$

Substitution and Mobility.—The previous investigation relating to the effect of *p*-substitution on mobility in the system (I $\rightleftharpoons$ II) afforded a sequence, *p*-NMe$_2$<*p*-Me<*p*-OMe<*p*-Hals., identical with the order of the dipole moments R–Ph, and therefore dependent

primarily upon inductive effects $(\pm I)^{*}$. The influence of the same p-substituents on side-chain reactivity of type B, exemplified by the velocity coefficients for the alkaline hydrolysis of p-substituted ethyl benzoates (Kindler, *Annalen*, 1926, **450**, I) and of p-substituted benzamides (Reid, *Amer. Chem. J.*, 1900, **24**, 403), conformed to the different sequence p-NMe$_2$<p-OMe<p-Me<p-Hals. (Table I). Reasons were given to show that the electromeric effect $(+ T)$ would operate in side-chain reactions of the type studied by Kindler and Read, but not in simple triad tautomeric systems such as (I $\rightleftharpoons$ II).

Certain facts, *e.g.*, the weak basicity of aniline, and the abnormally large dipole moments found for p-nitroaniline and p-nitroanisole, have led to the suspicion, now a very definite probability, that the electromeric effect $(\pm T)$ possesses a permanent component (compare Ingold and Shaw, J., 1927, 2918; Lapworth and Manske, J., 1928, 2534; *Ann. Reports*, 1929, **26**, 132; Ingold, Lapworth, Rothstein, and Ward, J., 1931, 1960). Apart from this, however, the chemical evidence adduced by Ingold and Patel (*J. Indian Chem. Soc.*, 1930, **7**, 95) and the physical evidence furnished by Sutton (*Proc. Roy. Soc.*, 1931, *A*, **133**, 668) form a consistent whole, and show that the electromeric effect in the aromatic nucleus must influence reactivity in the m-position.

Because the damping factor is very great, it is to be anticipated that facilitation of side-chain reactivity of type B by m-substituents will follow more closely the order of the dipole moment than was the case for facilitation by the same substituents in the p-position. That this expectation is realised is shown by the velocity coefficients for alkaline hydrolysis of m-substituted ethyl benzoates (Kindler, *loc. cit.*; *ibid.*, 1927, **462**, 90), m-substituted benzamides (Reid, *loc. cit.*), and m-substituted phthalides (Tasman, *Rec. trav. chim.*, 1927, **46**, 653, 922) (Table II).

TABLE I.

p-Substituent	NH$_2$	OMe	Me	(H)	Cl	Br	I
$k \times 10^3$ (Kindler)	1·1	10·5	23	49	212	242	249
$k \times 10^3$ (Reid)	18	46	62	94	180	180	159

TABLE II.

m-Substituent	NH$_2$	Me	(H)	OMe	Cl	Br	I	$\overset{\oplus}{N}\overset{O^{\ominus}}{\diagdown_{O}}$
$k \times 10^3$ (Kindler)	20	35	49	59	363	395	—	3110
$k \times 10^3$ (Reid)	—	75	94	—	—	282	245	530
$k \times 10^4$ (Tasman)	7·5	—	12	—	33	38	49	260

Experimental investigation of the influence of m-substitution on mobility in the system (I $\rightleftharpoons$ II) has now yielded the results sum-

* Really $\pm (I + D)$: compare Ingold, Lapworth, Rothstein, and Ward, *loc. cit.*

marised in Table III ; for convenience, the mobilities conferred by the same substituents in the p-position are included.

<div align="center">TABLE III.</div>

Substituent	NMe$_2$	Me	OMe	I	Br	Cl	$\overset{\oplus}{N}{\underset{O}{\overset{O\ominus}{\lessgtr}}}$
$k_1 + k_2$ meta (hrs.$^{-1}$)...	0·606	1·10	2·51	7·33	9·47	10·7	147
$k_1 + k_2$ para (hrs.$^{-1}$) ...	0·054	0·322	0·557	6·82	7·09	7·83	—
Dipole moment of R– C$_6$H$_5$ (E.S.U.$\times 10^{-18}$)	1·39	0·50	−0·80	−1·30	−1·49	−1·56	−3·90

It will be seen that once again the mobility sequence follows the order of the dipole moment (compare Shoppee, J., 1930, 968; 1931, 1226).

Comparison of Tables I, II, and III shows that the analogy, previously emphasised, between side-chain reactivity of type B and mobility is closer in the meta-series than in the para-series, which is consistent with theoretical expectation. The methyl and the dimethylamino-group $(+ I)$ must depress reactivity more in the p-position than in the m-position, as is found ; but in the case of the dimethylamino-group $(+ I + T)$ there is a second reason, namely, its possession of unshared electrons. All the other groups examined $(- I + T)$ should enhance reactivity in the m-position were it not for their unshared electrons, and it is to the possession of these that the inverse result must be attributed. Since the electromeric effect $(+ T)$ decreases in the order NR$_2$>OR>I> Br>Cl, it might be anticipated that the meta-para ratio of reactivity should decrease in the same order. For side-chain reactivity, using Kindler's values, the following figures are obtained :

Substituent	NMe$_2$	OMe	I	Br	Cl
k_m/k_p	18	5·6	—	1·6	1·7

whilst for mobility in the system $(I \rightleftharpoons II)$, the meta-para reactivity ratio similarly varies in a roughly regular way with basicity :

| Substituent	NMe$_2$	OMe	I	Br	Cl
$(k_1 + k_2)_m/(k_1 + k_2)_p$ ...	11·2	4·5	1·1	1·3	1·4

It appears impossible yet to advance any satisfactory explanation of the inversion of the halogens among themselves as found in the side-chain reactivity series (compare Tables I and II). No such inversion occurs in the mobility sequences.

Equilibrium and Substitution.—The equilibria attained by the system $(I \rightleftharpoons II)$, on introduction of the various m-substituents examined, are as follows :

m-Substituent, R	$\overset{\oplus}{N}{\underset{O}{\overset{O\ominus}{\lessgtr}}}$	NMe$_2$	Me	OMe	(H)	I	Br	Cl
K	0·47	0·58	0·66	0·83	1·00	1·35	1·74	1·82
Isomeride (I), %	68·0	63·0	60·0	54·7	50·0	42·5	36·5	35·5

According to the original simple view (*Ann. Reports*, 1927, **24**, 106; J., 1931, 1227) of the factors controlling equilibrium in simple triad prototropic systems, these results are clearly anomalous; for the expected order of the remaining groups relative to nitroxyl is inverted.

More thorough theoretical treatment of the factors controlling equilibrium led to the successful analysis of inverted equilibrium sequences resulting from *p*-substitution, by reference to the series which expresses the order in which groups in competition would control aromatic hydrogen substitution in the *op*-position (J., 1931, 1227). In the present case, analogy suggests the application of a

FIG. 1.

m-*Mobilities.*

$\log (k_1 + k_2)$.
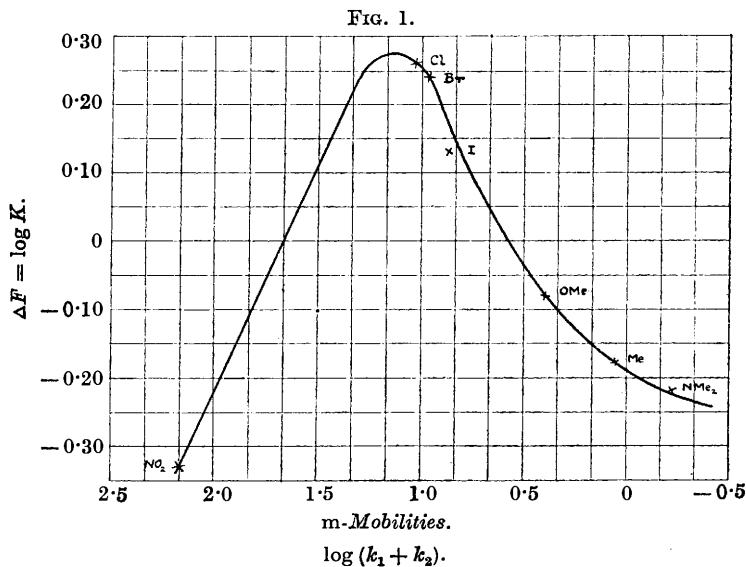
series composed of groups arranged in order according to the degree to which they would control competitive substitution in the *m*-position. Unfortunately, with the exception of nitroxyl, all the groups studied in the present work are *op*-orienting, and such a series has not yet been determined. In the absence of knowledge of the relative *m*-orienting effects of *op*-orienting groups, the only possible basis for comparison is side-chain reactivity.

The same factors which affect *m*-reactivity in the presence of *op*-orienting groups (the inductive effect and the permanent part of the electromeric effect) are also concerned in the *m*-direction of side-chain reactivity, although it is uncertain whether the two contributing factors are weighted in the same way in the two cases. Since mobility in tautomeric systems of the type under discussion

A A 3

may be regarded as a manifestation of side-chain reactivity, the mobility sequence for m-substituents, determined in the present work, suggests itself as the most practicable, even though not theoretically perfect, basis for comparison. Adopting this plan, a smooth curve, possessing a single maximum, is obtained (Fig. 1) which necessarily omits the point for hydrogen.

It is recognised that because of the imperfection of the foregoing comparison, further work may reveal minor discrepancies. Nevertheless it seems clear from the position of the maximum in Fig. 1 that, as in the case of the p-substituted compounds (Fig. 2,* J., 1931, 1229), the various m-substituted compounds differentiate themselves mainly by the relative stabilities of their ions rather than by the relative stabilities of the molecules.

<div align="center">E X P E R I M E N T A L.</div>

(Analyses marked * were carried out by Dr.-Ing. A. Schoeller.)

(A) *Preparation of Aldehydes.*—m-Tolualdehyde was prepared from m-toluanilide † by the method of Gibson, Harihan, Menon, and Simonsen (J., 1926, 2247), stannous chloride which had been dehydrated by treatment with acetic anhydride (Stephen, J., 1930, 2786) being used; m-chloro- and m-bromo-benzaldehyde were the best products supplied by British Drug Houses Ltd., and m-iodobenzaldehyde was obtained from m-aminobenzaldehyde by the Sandmeyer reaction. m-Anisaldehyde was prepared by methylation of pure m-hydroxybenzaldehyde (Kahlbaum) with methyl sulphate.

m-Dimethylaminobenzaldehyde was prepared according to instructions kindly supplied by Prof. A. Lapworth, F.R.S., who will publish details of the process in the near future. m-Nitrobenzaldehyde was supplied by British Drug Houses Ltd.

All the above aldehydes, which are liquid at the ordinary temperature, gave crystalline bisulphite compounds, which were isolated as a stage in the preparative process, and fractionation was carried out in an atmosphere of carbon dioxide. m-Iodo- and m-nitro-benzaldehyde were crystallised several times from alcohol and benzene respectively.

(B) *Preparation of Amines.*—Reduction of m-toluonitrile by the Ladenburg method furnished only a poor yield of impure m-methyl-

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* Fig. 2 (J., 1931, 1229) is numerical on one axis and only symbolical on the other. The numerical ordinate values (ΔF) were inadvertently omitted and were calculated from the experimentally determined values of the equilibrium constants K (J., 1930, 974; *loc. cit.*) by the relation $\Delta F = \log K$.

† m-Toluic acid with thionyl chloride readily affords the chloride, which gives m-*toluanilide*. prisms from dilute alcohol, m. p. 126° (Found : C, 79·3; H, 6·5. $C_{14}H_{13}ON$ requires C, 79·6; H, 6·2%).

benzylamine (compare Sommer, *Ber.*, 1900, **33**, 1074); the base was therefore obtained by reduction of *m*-tolualdoxime with 3% sodium amalgam in the presence of acetic acid. *m*-Tolualdoxime was used by Goldschmidt (*Z. Elektrochem.*, 1908, **14**, 581), but neither properties nor analyses are recorded by him; prepared from pure *m*-tolualdehyde by the method of Bamberger and Scheutz (*Ber.*, 1901, **34**, 2024), the oxime is a colourless liquid, b. p. 137°/17 mm., which readily crystallises and separates from ligroin (b. p. 40—60°) in prisms, m. p. 60° (Found * : C, 71·2; H, 6·8. Calc. for C_8H_9ON : C, 71·1; H, 6·7%). *m*-Methylbenzylamine was purified by conversion into the carbamido-derivative, which was crystallised to constant m. p. 148° (compare Sommer, *loc. cit.*); the regenerated base boiled constantly at 96°/20 mm. [picrate, m. p. 198° (decomp.) after crystallisation from methyl alcohol (Found * : C, 48·0; H, 4·2. Calc. for $C_{14}H_{14}O_7N_4$: C, 48·0; H, 4·0%); *benzoate*, needles from chloroform–ligroin (b. p. 40—60°), m. p. 150—150·5° (Found : C, 74·4; H, 7·2. $C_{15}H_{17}O_2N$ requires C, 74·05; H, 7·0%)]. An attempt to apply this method of purification to the halogenobenzyl-amines was unsuccessful owing to the extreme hydrolytic stability of the carbamido-derivatives.

m-Chlorobenzylamine, b. p. 111—112°/18 mm. [picrate, m. p. 204° (decomp.); *carbamido*-derivative, needles from dilute methyl alcohol, m. p. 129° (Found * : C, 51·5; H, 4·9. $C_8H_9ON_2Cl$ requires C, 52·0; H, 4·9%); compare v. Braun, Kühn, and Weismantel, *Annalen*, 1926, **449**, 266], was prepared by reduction of pure *m*-chloro-benzaldoxime, m. p. 70°, with 3% sodium amalgam in the presence of acetic acid. Under the same conditions pure *m*-bromobenzald-oxime, m. p. 71°, gave a product whose higher fraction, b. p. 120—125°/20 mm., contained 34—35% of benzylamine according to analyses of the picrate, m. p. 203° (decomp.) (Found : C, 40·6; H, 2·7%), and the benzoate, m. p. 132° (Found : C, 61·1; H, 4·9%), whilst *m*-iodobenzaldoxime yielded only benzylamine.

m-Bromobenzylamine was obtained by Gabriel's method; *m*-bromobenzyl bromide, m. p. 41°, prisms from ligroin (b. p. 40—60°) (Jackson, *Ber.*, 1876, **9**, 932), was condensed with potassium phthalimide at 180° to yield *phthalo-m-bromobenzylimide*, m. p. 138—139° after crystallisation from glacial acetic acid (Found : C, 56·8; H, 3·2. $C_{15}H_{10}O_2NBr$ requires C, 57·0; H, 3·2%), which by fission with hydrazine hydrate (Ing and Manske, J., 1926, 2348) afforded the base as a water-clear liquid, b. p. 126—127°/18 mm. [*picrate*, needles from alcohol, m. p. 205° (decomp.) (Found * : C, 38·0; H, 2·8. $C_{13}H_{11}O_7N_4Br$ requires C, 37·6; H, 2·7%); *benzoate*, laminæ from chloroform–ligroin, m. p. 135·5° (Found * : C, 54·5; H, 4·6. $C_{14}H_{14}O_2NBr$ requires C, 54·5; H, 4·6%); *carbamido-*

derivative, m. p. 132°, needles from dilute methyl alcohol (Found * : C, 42·1; H, 4·0. $C_8H_9ON_2Br$ requires C, 41·9; H, 3·9%); hydro-chloride, m. p. 216—217°].

m-Iodobenzylamine was prepared similarly; *m*-iodotoluene (65 g.) was treated with bromine (1 mol.) at 180°, and the semi-solid mass obtained on cooling was drained on porous plates and crystallised from ligroin (b. p. 40—60°), from which m-*iodobenzyl bromide*, m. p. 49—49·5°, separated in colourless prisms (24 g.) (Found * : C, 28·6; H, 2·3. C_7H_6BrI requires C, 28·3; H, 2·0%). Condensation of the last-named compound with potassium phthalimide at 180° furnished *phthalo*-m-*iodobenzylimide* (19 g.), m. p. 143·5° after crystallisation from acetic acid (Found * : C, 49·9; H, 3·1. $C_{15}H_{10}O_2NI$ requires C, 49·6; H, 2·8%), together with traces of a *substance*, m. p. 228°, which sublimed and separated from glacial acetic acid in rect-angular plates (Found * : C, 64·7; H, 3·6%). Fission of the imide with hydrazine hydrate gave *m*-iodobenzylamine as a water-clear liquid (5 g.), b. p. 132°/8 mm. [*picrate*, m. p. 210° (de-comp.), long needles from hot alcohol (Found * : C, 34·0; H, 2·6. $C_{13}H_{11}O_7N_4I$ requires C, 33·7; H, 2·6%); *benzoate*, m. p. 132°, laminæ from chloroform–ligroin (Found * : C, 47·6; H, 4·4. $C_{14}H_{14}O_2NI$ requires C, 47·3; H, 4·0%); *acetyl* derivative, m. p. 114·5°, long needles from ligroin (b. p. 80—100°) (Found * : C, 39·7; H, 4·0. $C_9H_{10}ONI$ requires C, 39·3; H, 3·7%); *carbamido*-deriv-ative, m. p. 170—171°, needles from methyl alcohol (Found * : C, 35·0; H, 3·4. $C_8H_9ON_2I$ requires C, 34·8; H, 3·3%)].

Oximation of *m*-anisaldehyde (compare Bamberger and Scheutz, *loc. cit.*) gave m-*anisaldoxime* as a thick water-clear liquid (10 g.), b. p. 170°/26 mm. (Found * : C, 63·8; H, 6·2. $C_8H_9O_2N$ requires C, 63·6; H, 6·0%), which by reduction with sodium amalgam and acetic acid afforded *m*-methoxybenzylamine, b. p. 103—104°/6 mm., as a colourless mobile liquid (5 g.) [*picrate*, m. p. 181°, prisms from methyl alcohol (Found * : C, 46·0; H, 3·95. $C_{14}H_{14}O_8N_4$ requires C, 45·6; H, 3·8%); *benzoate*, m. p. 95°, needles from chloroform–ligroin (Found * : C, 69·5; H, 6·7. $C_{15}H_{17}O_3N$ requires C, 69·5; H, 6·6%); p-*nitrobenzoyl* derivative, m. p. 124°, needles from methyl alcohol (Found * : C, 63·0; H, 5·05. $C_{15}H_{14}O_4N_2$ requires C, 63·0; H, 4·9%)]. An attempt was made to employ electrolytic reduction (compare Kindler, D.R.-P. Anmeld. *K*. 85,210) of m-*methoxybenz-amide*, m. p. 133° (Found : C, 63·4; H, 6·0. $C_8H_9O_2N$ requires C, 63·6; H, 6·0%), but the foregoing method was found more convenient for small quantities of the base.

From *m*-dimethylaminobenzaldoxime, by reduction with sodium amalgam and acetic acid, *m*-dimethylaminobenzylamine, b. p. 134—135°/10 mm., was obtained as a colourless mobile liquid [*mono-*

picrate, deep red prisms from methyl alcohol, m. p. 206° (decomp.) (Found * : C, 47·6; H, 4·55. $C_{15}H_{17}O_7N_5$ requires C, 47·5; H, 4·5%); *dipicrate*, yellow prisms from methyl alcohol, m. p. 170° (Found * : C, 41·6; H, 3·4. $C_{21}H_{20}O_{14}N_8$ requires C, 41·4; H, 3·3%); *benzoate*, felted needles from chloroform–ligroin, m. p. 111·5° (Found : C, 69·6; H, 7·6. $C_{16}H_{20}O_2N_2$ requires C, 70·6; H, 7·5%)].

Phthalo-*m*-nitrobenzylimide, m. p. 160·5° (compare Gabriel and Hendes, *Ber.*, 1887, **20**, 2869), by fission with hydrazine hydrate, gave *m*-nitrobenzylamine. The base was purified by conversion into the picrate, which was crystallised to constant m. p. 202° and regeneration therefrom.

(C) *Preparation of Azomethines.*—This was carried out by the method previously described (J., 1931, 1225), or by condensation of the components in ethereal solution and removal, as the carbonate, of the slight excess of amine employed by passage of carbon dioxide, with subsequent drying and evaporation.

A high degree of purity is necessary to afford satisfactory kinetic measurements. For the purification of solid azomethines, crystallisation to constant m. p. from suitable solvents was employed : liquid azomethines were repeatedly fractionated from Claisen flasks incorporating fractionating columns. The azomethines were used as soon as possible after preparation, since they tend to decompose on keeping, particularly those which are liquid; they may be preserved satisfactorily for several days in a vacuum over solid potassium hydroxide.

m-*Methylbenzylidenebenzylamine* (as I) is a colourless water-clear liquid, b. p. 187°/12 mm. (Found * : C, 85·6; H, 7·2. $C_{15}H_{15}N$ requires C, 86·1; H, 7·2%). *Benzylidene-*m-*methylbenzylamine* (as II) has b. p. 170°/7 mm. (Found * : C, 85·7; H, 7·3%).

m-*Chlorobenzylidenebenzylamine* is an almost colourless liquid, b. p. 190°/10 mm. (Found * : C, 73·2; H, 5·3. $C_{14}H_{12}NCl$ requires C, 73·4; H, 5·3%). *Benzylidene-*m-*chlorobenzylamine* has b. p. 175°/5·5 mm. (Found * : C, 72·9; H, 5·3%).

m-*Bromobenzylidenebenzylamine* was first obtained as a faintly yellow liquid, b. p. 200°/10 mm., solidifying to a mass of prismatic needles, m. p. 32°, which after recrystallisation from methyl alcohol had m. p. 34·5°, but did not furnish satisfactory analytical figures (Found : C, 64·9, 64·7 *; H, 4·7, 4·6 *; N, 4·5 *; Br, 25·0.* $C_{14}H_{12}NBr$ requires C, 61·3; H, 4·4; N, 4·4; Br, 29·2%). A specimen of *m*-bromobenzaldehyde was further purified by conversion into the *semicarbazone*, which was crystallised from methyl alcohol to a constant m. p. 228° (decomp.) (Found * : C, 40·8; H, 3·4. $C_8H_8ON_3Br$ requires C, 39·7; H, 3·3%). The azomethine obtained from the regenerated aldehyde had m. p. 38°

after repeated crystallisation from methyl alcohol (Found : C, 62·6,*
63·0; H, 4·3,* 4·8%). *Benzylidene*-m-*bromobenzylamine* has b. p.
217—218°/15 mm. (Found : C, 61·1; H, 4·4%).

m-*Iodobenzylidenebenzylamine* is a colourless solid, m. p. 73° after
repeated crystallisation from methyl alcohol (Found : C, 52·3;
H, 3·9. $C_{14}H_{12}NI$ requires C, 52·3; H, 3·7%). *Benzylidene*-m-
iodobenzylamine is a colourless oil, b. p. 220—221°/12 mm. (Found * :
C, 53·0; H, 4·1%).

m-*Methoxybenzylidenebenzylamine* is a colourless oil, b. p. 206°/
15 mm. (Found * : C, 79·8; H, 6·7. $C_{15}H_{15}ON$ requires C, 80·0;
H, 6·6%). *Benzylidene*-m-*methoxybenzylamine*, b. p. 186°/6 mm.,
readily crystallises and separates from ligroin (b. p. 40—60°) in
rectangular prisms, m. p. 37° (Found * : C, 79·8; H, 6·7%).

m-*Dimethylaminobenzylidenebenzylamine* is a yellow oil, b. p.
223°/10 mm. (Found * : C, 80·2; H, 7·6. $C_{16}H_{18}N_2$ requires C,
80·6; H, 7·6%). *Benzylidene*-m-*dimethylaminobenzylamine* is a
faintly yellow oil, b. p. 200°/5 mm. (Found * : C, 80·6; H, 7·6%).

m-Nitrobenzylidenebenzylamine had the m. p. (62°) and properties
described by Ingold and Piggott (J., 1922, 2385); benzylidene-m-
nitrobenzylamine had m. p. 32·5—32·7° after repeated crystallis-
ation from methyl alcohol, whilst an independent preparation by Mr.
C. L. Wilson, M.Sc., gave a specimen, m. p. 32°; it seems probable
that the m. p. (42°) recorded by Ingold and Piggott is a misprint.

ω-*Benzylimino*-m-*tolyltrimethylammonium Iodide* (as I).—The salt
may be obtained by warming m-dimethylaminobenzylidenebenzyl-
amine with methyl iodide (1 mol.), or by treatment of m-aldehydo-
phenyltrimethylammonium iodide in alcoholic suspension with
benzylamine (1 mol.). After crystallisation from acetone–ether
it has m. p. 128—129° (Found : C, 51·5; H, 5·8; I, 34·5. $C_{17}H_{21}N_2I$
requires C, 53·7; H, 5·6; I, 33·4%).

ω-*Benzylideneamino*-m-*tolyltrimethylammonium iodide* (as II) is
readily obtained from benzylidene-m-dimethylaminobenzylamine
by treatment with methyl iodide (1 mol.) and crystallises from
methyl alcohol–ether; m. p. 145—146° (Found : I, 33·6%).

(D) *Interconversion of Tautomerides.*—The standard conditions
employed for the interconversion of azomethines were : catalyst,
0·145N-alcoholic sodium ethoxide; temperature, 82°. The product
was isolated as previously described (J., 1931, 1225). To follow the
progress of interconversion, the method involving thermal analysis
of mixtures of p-nitrophenylhydrazones was used. The p-nitro-
phenylhydrazones obtained from derivatives of the halogen-, meth-
oxyl-, and nitro-substituted benzaldehydes appear to occlude traces
of foreign matter, since the yields are 2—4 units above 100%;
whatever the nature of the impurity, it exercises little or no influence

on the m. p. of the hydrazone (compare table below), and any error thus introduced is minimised by use of the hydrazones without further purification for the construction of temperature–composition diagrams. All such diagrams were of the two-branch type, and the products of the interconversion experiments strictly binary in character. All m. p.'s given are uncorrected, but were determined under identical conditions in the same apparatus.

The table gives the m. p.'s, yields obtained by decomposition of azomethines (I) with p-nitrophenylhydrazine, and analytical data for the following m-substituted benzaldehyde-p-nitrophenylhydrazones :

	M. p. (purif.).	M. p. (crude).	Yield, %.	Found. C, %.	Found. H, %.	Calc., C, %.	Calc., H, %.
m-*Methyl*-	157°	157°	100·5	65·7*	5·3*	65·9	5·1
m-*Chloro*-	214	214	102	56·8*	3·7*	56·7	3·7
m-*Bromo*-†	220·5	220	104	50·4, 51·0*	3·4, 3·4*	48·8	3·2
m-*Iodo*-	208	206·5	104	42·4	2·9	42·5	2·75
m-*Methoxy*-	171	169	104	61·8	5·0	61·9	4·9
m-*Dimethylamino*‡	190	188	100·5	63·3*	5·5*	63·4	5·7
m·Nitro-	248	248	103	—	—	—	—

† M. p. unchanged by further crystallisation.
‡ Slightly soluble in 10% acetic acid.

The following observations were used for the construction of temperature–composition diagrams; in each case A refers to benzaldehyde-p-nitrophenylhydrazone.

m-*Tolualdehyde-p-nitrophenylhydrazone and A* :

A, % ...	0	14·7	24·7	30·5	36·1	46·8	55·5	65·7	84·0	100
M. p. ...	157°	152°	148·5°	148°	154°	162°	167·5°	173°	182·7°	190°

m-*Chlorobenzaldehyde-p-nitrophenylhydrazone and A* :

A, % ...	0	16·0	27·7	46·5	60·5	62·5	72·0	80·7	100
M. p. ...	214°	206°	200°	189°	178·5°	177°	179°	182·5°	190°

m-*Bromobenzaldehyde-p-nitrophenylhydrazone and A* :

A, % ...	0	16·0	28·2	46·0	58·0	63·5	72·0	86·0	100
M. p. ...	220·5°	210°	203°	192°	182°	176°	176°	184·5°	190°

m-*Iodobenzaldehyde-p-nitrophenylhydrazone and A* :

A, % ...	0	20·4	39·8	45·4	50·0	56·9	67·8	80·4	100
M. p. ...	206·5°	196°	182°	178·5°	175·5°	171°	175°	182°	190°

m-*Anisaldehyde-p-nitrophenylhydrazone and A* :

A, % ...	0	21·2	34·6	40·1	45·3	47·5	48·2	57·2	63·9	77·7	100
M. p.	169°	159°	157·5°	148·5°	147·5°	154°	154·5°	163°	168·5°	177°	190°

m-*Dimethylaminobenzaldehyde-p-nitrophenylhydrazone and A* :

A, % ...	0	18·9	29·3	33·4	35·6	38·8	43·9	56·5	75·4	100
M. p. ...	188°	174°	167°	163·5°	161·5°	158·5°	156°	164·5°	176°	190°

m-*Nitrobenzaldehyde-p-nitrophenylhydrazone* and A :

A, % ...	0	21·0	32·0	38·2	59·1	69·0	81·1	100
M. p. ...	248°	234·5°	227°	223°	206°	190°	179·5°	189·5°

* This hydrazone melts without decomposition, but commences to decompose when maintained at or above the m. p.

(E) *Determination of Mobility and Equilibrium.*—

m-*Methylazomethines* :

Isomeride used.	Time with NaOEt at 82° (hrs.).	Yield, %.	M. p.	Isomeride (II), %.	$k_1 + k_2$ (hrs.$^{-1}$).
I	0	100·5	157·0°	0	—
	0·5	99·3	151·0	17·5	1·15
	1·0	99·0	147·0	29	1·29
	1·5	99·0	150·0	·32	1·07
	2·0	98·0	157·0	40	—
	3·0	97·5	157·0	40	—
	4·5	97·0	157·0	40	—
II	4·0	97·5	157·0	40	—
	3·0	97·5	160·5	44·5	(0·86)
	2·0	99·2	163·0	48	1·01
	1·0	98·3	172·5	64	0·92
	0·5	99·7	178·0	74·5	1·08
	0·25	99·8	183·3	85	1·15
	0	100	190·0	100	—

Equilibrium : II (40·0) $\rightleftharpoons$ I (60·0); $k_1 + k_2$ (mean) $= 1\cdot10$ hrs.$^{-1}$; $k_1/k_2 = 0\cdot666$; $k_1 = 0\cdot440$; $k_2 = 0\cdot660$.

In view of the theoretical importance of the equilibrium ratio in this case, the equilibrium attained in the presence of $1\cdot45N$-alcoholic sodium ethoxide at 85° was determined :

Isomeride used.	Time with NaOEt at 85° (hrs.).	M. p.	Isomeride (II), %.
I	1·0	157·0°	40
	1·0	157·0	40
II	0·75	156·5	39
	1·0	157·0	40

m-*Chloroazomethines* :

Isomeride used.	Time with NaOEt at 82° (mins.).	Yield, %.	M. p.	Isomeride (II), %.	$k_1 + k_2$ (hrs.$^{-1}$).
I	0	102, 102	214·0°	0	—
	2	101	204·0	19·5	10·58
	4	101	198·0	31·5	10·00
	5	—	195·0	37	10·21
	6	101	191·5	42	10·52
	8	101	187·0	49·5	10·39
	10	100	185·0	52·5	10·04
	15	101	179·0	60	10·63
	20	—	175·0	64·5*	—
	30	100	175·0	64·5*	—
I	25	97	175·5	64·5*	—
	10	100	177·5	69	(12·38)
	9	99	178·7	71·5	10·81
	7	100	179·5	74	11·30
	6	—	180·5	76	11·28
	5	100·5	181·3	78	11·59
	4	100·5	182	80	(12·43)
	3	100	184	85	10·98
	2	100	185·5	89	11·13
	1	—	187·7	94	11·11
	0	100	190·0	100	—

* This is also the eutectic mixture.

Equilibrium : II (64·5) $\rightleftharpoons$ I (35·5): $k_1 + k_2$ (mean) $= 10\cdot75$ hrs.$^{-1}$; $k_1/k_2 = 1\cdot817$; $k_1 = 6\cdot94$; $k_2 = 3\cdot81$.

m·*Bromoazomethines* :

Isomeride used.	Time with NaOEt at 82° (mins.).	Yield, %.	M. p.	Isomeride (II), %.	$k_1 + k_2$ (hrs.$^{-1}$).
	0	104, 104	220°	0	—
	2	100	208	17·5	9·76
	3	98	205	24	9·47
	4	99	202	29	9·13
	5	100	199	34·5	9·38
I	6	99	196, 196	39	9·51
	8	99	191·5	46·5	9·87
	9	98	190	48·5	9·60
	10	—	188	51	9·83
	15	100	182	58	9·76
	20	—	179·5	60·5	9·11
	30	100	176	63·5	—
	35	99	176 *	63·5	—
	15	98	175·5	70·5	(6·31)
	8	98	178	75	8·64
II	6	99	180	78	9·21
	4	98	182·5	83	9·37
	2	99	186	89·5	10·15
	0	100	190	100	—

* To 8·4 mg. of the equilibrium specimen, 1·2 mg. of *m*-bromobenzaldehyde-*p*-nitrophenylhydrazone were added : the resulting mixture had m. p. 183°; calculated, m. p. 184°.

Equilibrium : II (63·5) $\rightleftharpoons$ I (36·5) : $k_1 + k_2$ (mean) = 9·47 hrs.$^{-1}$; $k_1/k_2 = 1·74$; $k_2 = 6·01$; $k_2 = 3·46$.

m·*Iodoazomethines* :

Isomeride used.	Time with NaOEt at 82° (mins.).	Yield, %.	M. p.	Isomeride (II), %.	$k_1 + k_2$ (hrs.$^{-1}$).
	0	104, 104	206·5°	0	—
	1	101	204	6·5	7·20
	2	100	200·5	12·5	7·35
	3	100	197·5	18	7·49
	4	100	194·5	22	7·22
	5	97	193	25·5	7·02
I	8	98	184	37·5	7·91
	10	98	182	40·5	7·30
	12	97	179	44·5	7·42
	14	—	177·5	46·5	7·22
	16	97	175	50	7·70
	22	97	173	53·5	—
	60	97	170·5	57·5	—
	60	—	170·5	57·5	—
	10	99	175·5	70	7·32
	8	—	177	73·5	7·30
II	6	99	181	78	7·13
	4	99	183·5	84	7·08
	2	98	186·5	91	7·13
	0	100	190	100	—

Equilibrium : II (57·5) $\rightleftharpoons$ I (42·5); $k_1 + k_2$ (mean) = 7·33 hrs.$^{-1}$; $k_1/k_2 = 1·35$; $k_1 = 4·21$; $k_2 = 3·12$.

m-*Methoxyazomethines* :

Isomeride used.	Time with NaOEt at 82° (mins.).	Yield, %.	M. p.	Isomeride (II), %.	$k_1 + k_2$ (hrs.$^{-1}$.).
	0	104, 104	169°	0	—
	5	103	164·5	9	2·66
	7·5	103	162·7	13	2·66
	10	102	161	17	2·78
	12·5	101	160	19·5	2·70
	15	101	159	21	2·50
I	20	100	157	25	2·40
	30	—	154	30	2·25
	60	100	148	41	—
	90	100	146·5	45·3	—
	120	100	147	45·3	—
	240	—	147	45·3	—··
	480	—	147	45·3	—
	180	99	147	45·3	—··
	90	97·5	152	46	—
	30	98	167·5	62	2·37
	20	99	173	71	2·27
II	18	98	174	72·5	2·33
	14	98	176	76	2·47
	10	98	179	81	2·56
	5	98	183·5	89	2·70
	0	100	190	100	—··

Equilibrium :　II　(45·3) $\rightleftharpoons$ I　(54·7);　$k_1 + k_2$　(mean) $= 2·51$　hrs.$^{-1}$; $k_1/k_2 = 0·828$;　$k_1 = 1·13$;　$k_2 = 1·38$.

Further to confirm the value found for the equilibrium ratio, new specimens of both isomerides were equilibrated in the presence of 1·45N-alcoholic sodium ethoxide at 85° :

Isomeride used.	Time with NaOEt at 85° (hrs.).	M. p.	Isomeride II, %.
I	0·5	147°	45·3
	0·75	147	45·3
II	0·5	147	45·3
	0·75	147	45·3

A synthetic mixture of azomethines in the proportion 55·1% (I) : 44·9% (II) was analysed : a 97% yield of *p*-nitro-phenylhydrazones was obtained, m. p. 147·5°; this m. p. corresponds to a mixture containing 54·7% (I) : 45·3% (II).

m-*Dimethylaminoazomethines* :

Isomeride used.	Time with NaOEt at 82° (hrs.).	Yield, %.	M. p.	Isomeride (II), %.	$k_1 + k_2$ (hrs.$^{-1}$).
	0	100·5	188°	0	—
	0·5	94	182	8	0·487
	1·0	93	178	14	0·476
I	1·5	—	173·5	20	0·519
	2·0	96·5	170·5	24	0·522
	7·0	93	160	37	—

Isomeride used.	Time with NaOEt at 82° (hrs.).	Yield, %.	M. p.	Isomeride (II), %.	$k_1 + k_2$ (hrs.$^{-1}$).
	7·0	92	160	37	—
	3·0	94	156·5	40	—
	2·5	94	153	42	—
	1·5	94, 94	164, 163·5	56	0·798
II	1·25	95	169	64	0·678
	1·0	94	172	69	0·676
	0·75	97	175·5	75	0·671
	0·5	94	181	84	0·584
	0·25	98	184·25	90·5	0·655
	0	100	189·5	100	—

Equilibrium : II (37) $\rightleftharpoons$ I (63); $k_1 + k_2$ (mean) = 0·606 hrs.$^{-1}$; k_1/k_2 = 0·587; k_1 = 0·224; k_2 = 0·382.

The equilibrium attained with 1·45N-sodium ethoxide at 85° was also determined by the following chemical method. Either azomethine was treated with the catalyst for 1 hour, and, after isolation in the usual way and addition of 2N-sulphuric acid, was steam-distilled in a current of carbon dioxide in a special all-glass apparatus: the distillate was collected in a receiver containing a solution of p-nitrophenylhydrazine acetate, and benzaldehyde present was estimated as the p-nitrophenylhydrazone.

Isomeride.	Wt. taken, g.	Wt. of hydrazone, g.	(II), %.
I	0·1005	0·0396	38·9
II	0·1073	0·0408	37·5
		Average	38·2

This result, II (38) $\rightleftharpoons$ I (62), is in good agreement with that determined by the physical method.

m-*Nitroazomethines* :

Isomeride used.	Time with NaOEt at 82° (secs.).	Yield, %.	M. p.	Isomeride (II), %.	$k_1 + k_2$ (hrs.$^{-1}$).
	0	103	248°	0	—
	5	—	244	6	149
I	10	—	240·5	11·5	160
	15	—	237	16	159
	30	—	230	28	—
	60	100	227	32	—
	60	—	197	65	—
	30	—	183	71	—
II	15	—	174	72	127
	10	—	177	78	141
	5	—	183	87·5	146
	0	101	189·5	100	—

[The data for isomeride (I) show that doubling the period of interconversion (from 30 to 60 seconds) leads to an increase of only 4% of (II); since some side-reaction accompanies the process of interconversion, as is clearly shown by the m. p. data for isomeride (II), which rise after passing the eutectic, but insufficiently fast to cor-

respond to a velocity constant $k_1 + k_2 = 150$ (approx.), the equilibrium could be approached only from the side of isomeride (I), and the apparent 4% increase of conversion mentioned above may be due partly or wholly to the progress of the side-reaction. It seems, however, fairly certain that the equilibrium ratio is close to II (30) $\rightleftharpoons$ I (70).] Equilibrium : II (32) $\rightleftharpoons$ I (68) : $k_1 + k_2$ (mean) = 147 : $k_1/k_2 = 0.47$: $k_1 = 47$; $k_2 = 100$.

Trimethylammoniumazomethines. The trimethylammoniumazomethines, in contrast to their *p*-isomerides (J., 1931, 1239), exhibit no tendency to eliminate methyl iodide. Thus the azomethine (I) by treatment with *p*-nitrophenylhydrazine acetate under the standard conditions gives a clear solution containing the salt (III); a *chloroplatinate*, m. p. 207—208° (decomp.), precipitated by addition of platinic chloride could not be crystallised from any solvent and was analysed crude (Found : Pt, 20·2. $C_{16}H_{20}O_2N_4Cl_6Pt$ requires Pt, 27·5%).

$$\text{(III.)} \quad Ac^{\ominus}\{(m)\overset{\oplus}{N}Me_3 \cdot C_6H_4 \cdot CH{:}N \cdot NH \cdot C_6H_4 \cdot NO_2 \ (p)$$
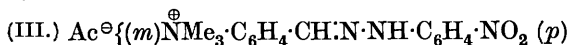
Moreover the azomethines (I, II) after brief treatment with 0·145 *N*-sodium ethoxide at 82° furnish clear solutions when the catalyst is destroyed by addition of excess of cold water, thereby indicating that they are still present as trimethylammonium salts.

Investigation by the chemical method outlined under dimethylamino-azomethines shows that rapid interconversion takes place in the presence of the catalyst, although only a few measurements could be made owing to scarcity of material. After destruction of the catalyst, the clear solution was washed into a special all-glass apparatus, and, after addition of $2N$-sulphuric acid (25 c.c.), benzaldehyde was estimated by steam-distillation in an atmosphere of carbon dioxide and conversion into the *p*-nitrophenylhydrazone.

Isomeride used.	Wt., g.	Time with NaOEt at 82° (secs.).	Wt. of $C_6H_5 \cdot CH{:}N \cdot NH \cdot C_6H_4 \cdot NO_2$.	Isomeride (II), %.
	0·1006	0	—	0
I	0·0870	30	0·0080*	15
	0·1047	60	0·0135†	20
	0·0995	30	0·0250	40
II	0·1002	10	0·0515	81
	0·1005	0	0·0637	100

* M. p. (crude) 185° : † m. p. (crude) 18·5° : in both cases mixed m. p. 186—187°.

No great accuracy is claimed for these figures, but it is evident that the *m*-$\overset{\oplus}{N}Me_3$ group confers a high degree of mobility, comparable with that conferred by the *m*-NO_2 group, and that the equilibrium largely favours isomeride (I).

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